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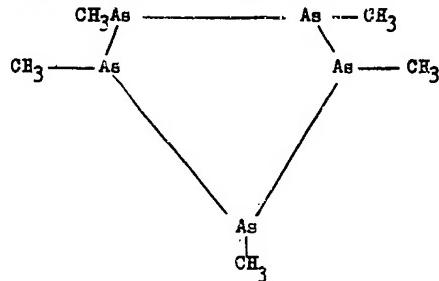
## POLYMERIC ARSENICAL COMPOUNDS

### POLYMERS OF ARSENIOMETHANE

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Arsenomethane was first prepared by Auger (1) by the reduction of methylarsinic acid with hypophosphorus acid. The compound is a yellow, oily substance with a BP of 190° at 15 mm. The molecular weight determination carried out by Auger (cryoscopically, in benzene) gave the value 300 - 34. On this basis Auger ascribed the formula  $(CH_3As)_4$  to this compound, which he called "methylarsinic."

Later, Bertheim (2), on the basis of certain reactions and analogies, ascribed the formula  $\text{CH}_2\text{As} = \text{AsCH}_2$ , to this compound and called it "arsenomethane." A more exact determination of molecular weight was carried out by Steinkopf (3), who obtained the values 428, 436 and therefore assigned the following cyclic structure to the compound:



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and called it "pentamethylmentarsine." The value for the molecular weight found by Steinkopf was later confirmed by Palmer (4).

Auger also noticed that this compound, which from now on we shall refer to as "arsenomethane" for the sake of simplicity, polymerizes very readily, forming a solid, intensely colored compound, insoluble in ordinary solvents, with the same summary formula. The physical properties of this compound (insolubility in ordinary solvents, and the fact that it does not melt without decomposing) indicate its great molecular weight. Auger gave this compound the formula  $(CH_3As)_n$ . The value of n is still unknown.

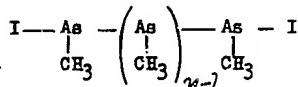
Evidently, there exists not one but a series of arsenomethane polymers as several polymers, differing considerably in external appearance (from orange to almost black), have been described in the literature (1,4). Up to now, these polymers have not been subjected to any detailed investigation. This is undoubtedly due to their physical properties -- insolubility in the ordinary solvents.

In the present paper our objective is to discover whether cyclic polymers are formed during the polymerization of arsenomethane, or whether polymerization is accompanied by the formation of an open chain of the main valencies.

For the solution of this problem we turned our attention to an observation of Auger, who remarked that polymerization of arsenomethane is considerably accelerated (caused ? M.K.) when it comes into contact with hydrochloric acid. We used this observation of Auger in the following manner:

If cyclic polymers are formed during the polymerization of arsenomethane, the composition of the polymer must be in exact correspondence with the formula  $CH_3As$ . If, on the other hand, an open chain of the main valencies is formed during polymerization, the composition of the polymer should not correspond to the simple formula, as it is to be expected that the polymer molecule will contain some end groups or atoms acting as end groups.

To demonstrate the presence of end groups in the polymer molecule, we brought about the polymerization of arsenomethane by the addition of diiodoarsine, reckoning that in this case the iodine atoms would act as end groups in the polymer molecule:



The choice was influenced by the high atomic weight of iodine, and the ease with which it can be determined.

The polymerization of arsenomethane was carried out in the following manner: 1.25 gm iodine (0.01 gm/at) was added to a solution of 3.6 gm arsenomethane (0.01 gm/mol) in 15 cc of dry benzene. The resultant solution was left for 2 days at room temperature (15 - 20°). After 2 days, the dark precipitate which had been deposited was filtered off and washed several times with benzene, alcohol and ether (solvents in which methylidoarsine is readily soluble); 1.5 gm of an almost black substance was obtained.

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0.1820 gm substance: 0.0185 gm AgI  
 0.1767 gm " 0.0178 gm AgI  
 0.1592 gm " 33.50 cc 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
 0.1472 gm " 31.1 cc 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
 Found %: I 5.49, 5.44; I 78.88, 79.18

The iodine content of the polymer obtained cannot be reduced by washing. Consequently, its content is not determined by adsorption phenomena, but by the fact that the iodine actually forms part of the polymer molecule. This is also indicated by the fact that even a sharp decrease in the amount of iodine taken for the reaction (1/100 !) makes no essential difference to the composition of the polymer obtained, merely decreasing the yield. On adding iodine to the filtrate, the arsenomethane polymer is produced as before.

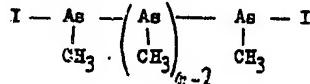
This data affords convincing evidence that the molecule of the arsenomethane polymer contains end groups (in the case given, their role is played by iodine atoms). Further evidence is provided by our experiments on arsenomethane polymerization using various amounts of solvent. As is well known (Staudinger), when polymerization takes place in more dilute solutions, the polymers obtained have a lower degree of polymerization, i.e., they contain a greater percentage of end groups.

It is natural that in the case of adsorption the reverse would hold good. The above experiment was carried out in 15 cc of benzene. If, with the initial quantities unchanged, the experiment is carried out in 50 cc of benzene, the polymer obtained contains 8.67% of iodine. A further increase in the quantity of benzene up to 160 cc leads to the formation of a polymer containing 9.06 percent of iodine.

It is easy to determine the degree of polymerization of the polymers prepared from their iodine content:

For a polymer with 9.05% I n = 27.10, mol weight = 2,693  
 " " " 8.67% I n = 29.73, mol weight = 2,930  
 " " " 5.47% I n = 48.76, mol weight = 4,343

Turning now to the conditions of polymerization, described by Auger, an interesting conclusion can be drawn: It is quite natural that a polymer of the structure



should contain as end groups either chlorine atoms (polymerization in the presence of HCl) or hydroxyl groups (polymerization was carried out in the presence of water). It is obvious that a polymer of this composition could be prepared from arsenomethane only in the presence of an oxidizing agent. Air alone may have been the oxidizer in Auger's experiments. One can readily conclude from what has been said that polymerization of arsenomethane cannot occur in the absence of air. In fact, if the possibility of oxidation of arsenomethane is completely excluded, it does not polymerize even in the presence of hydrochloric acid. As arsenomethane oxidizes very easily, this can best be achieved by adding a reducing agent to the hydrochloric acid mixture. Hypophosphorous acid is the most suitable for this purpose.

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Conclusions

1. Polymerization of arsrenomethane results in the formation of macromolecules of the general formula (I).
2. Polymers of arsrenomethane were prepared in which iodine atoms act as end groups.
3. It was shown that polymerization does not occur under conditions where end groups cannot be formed.

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